

REPORT DOCUMENTATION PAGE

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Update in Ionic Liquids Research

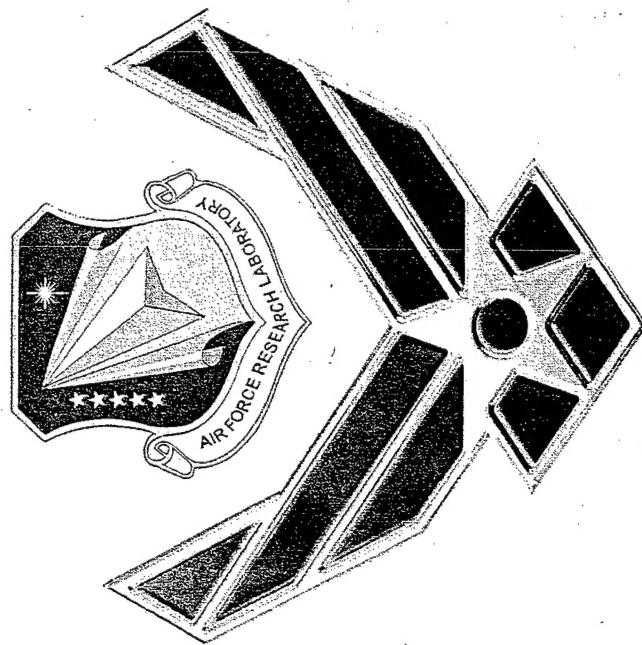
Greg Drake and Tommy Hawkins

AFRL/PRSP

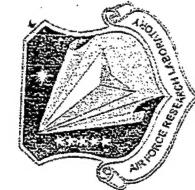
AFOSR Ionic Liquids Workshop

March 7 & 8, 2004

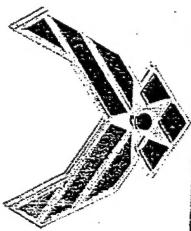
Tampa, FL



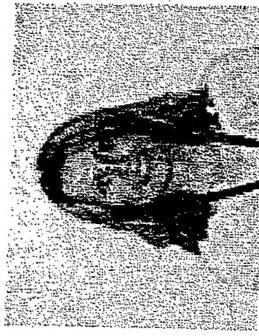
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AFRL Ionic Liquids



Those involved in this work



Ms. Kerri Tollison
Synthesis and
Characterization



Greg Kaplan
Synthesis and
Characterization



Jerry Boatz
Theoretical
Calculations



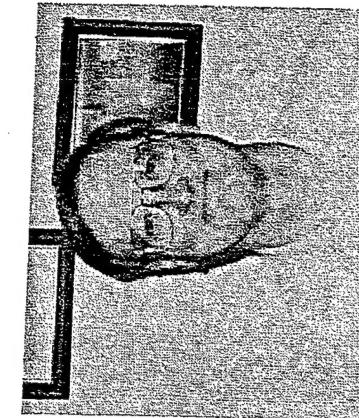
Jeff Mills
Theoretical
Calculations



Leslie Hall
Synthesis &
X-ray work



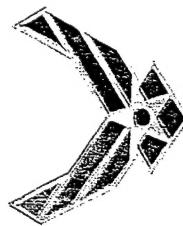
Ashwani Viji
X-ray
crystallography



Tommy Hawkins
6.2 Propellant
Development



Greg Drake
6.1 Research
Synthesis



AFRL Ionic Liquids

HOW WE GOT TO WHERE WE ARE

- SIMPLE SALTS USING PROTIC ACIDS

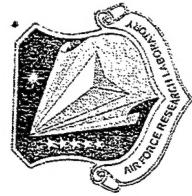
- OPEN CHAIN WORK
HYDROGEN BONDING EFFECTS

HYDRAZINE ANALOGUES

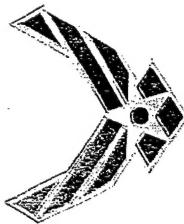
SOME SIMPLE AMINES

- HETEROCYCLIC APPROACH

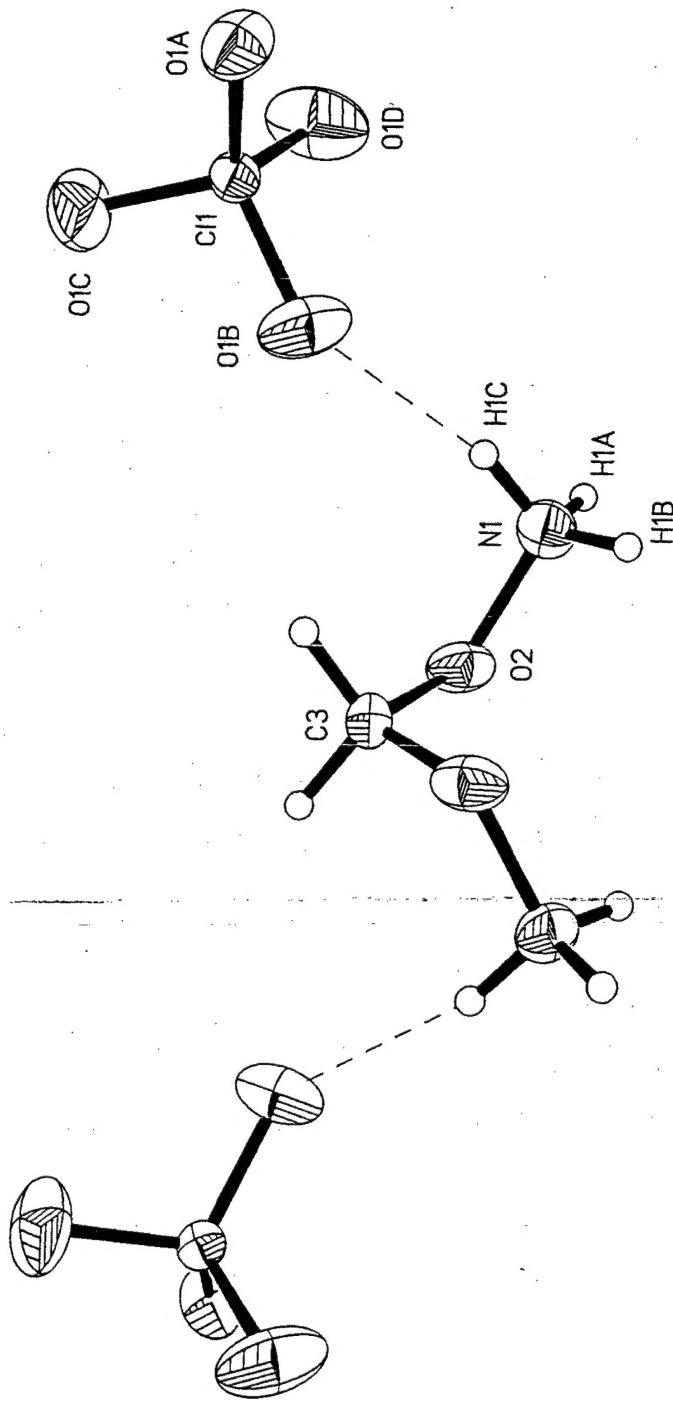
SHAPE CONSIDERATIONS

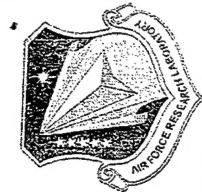


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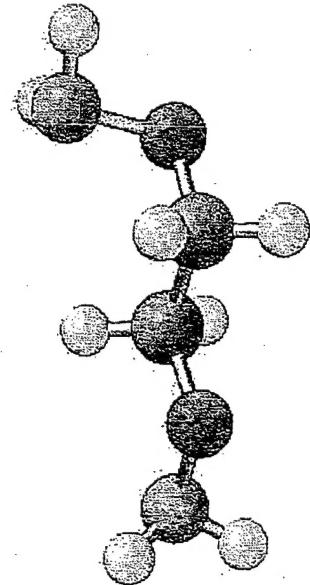
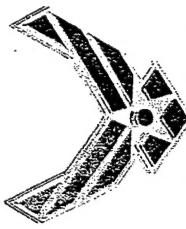


- Oxyamine, $-\text{O}-\text{NH}_2$, is analogue to hydrazine linkage $-\text{NH}-\text{NH}_2$
- $\text{CH}_2(\text{O}-\text{NH}_2)_2$ Explored at Edwards in late 1960's (Claude Merrill)
- Reinvestigation of mono- and di- salts
- Several of the salts met the definition of an ionic liquid
- Treacherous! Sensitive to mechanical stimuli! Explode unexpectedly!



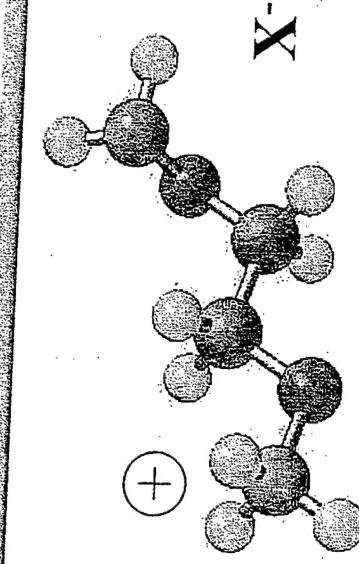
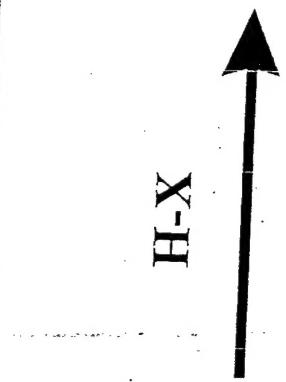


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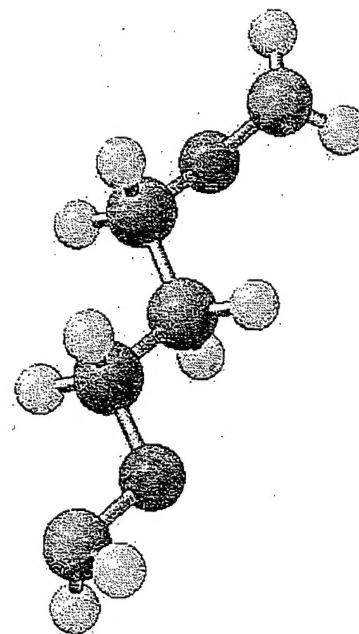


1,2-bis(oxyamine)ethane

Dixon, D. W.; Weiss, R. H. J Org. Chem. 1984, 49, 4487.



1,2-bis(oxyamine)ethane mono salts
 $X^- = NO_3^-$, ClO_4^- , $C(NO_2)_3^-$, $N(NO_2)_2^-$

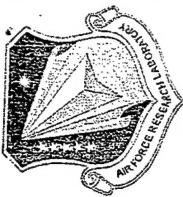


1,3-bis(oxyamine)propane very stable, watery liquid
b.p. = 65-70 C @ 0.3 torr; f.p. = glasses at -40 C
 $X^- = NO_3^-$, ClO_4^- , $C(NO_2)_3^-$, $N(NO_2)_2^-$

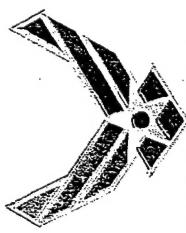
In either case, the oxyamines yield extremely friction and impact sensitive materials.

Drake, G.; Hawkins, T.; Hall, L.; Sheehy, J. Prop. Energ. Pyrotech. Submitted 2004.

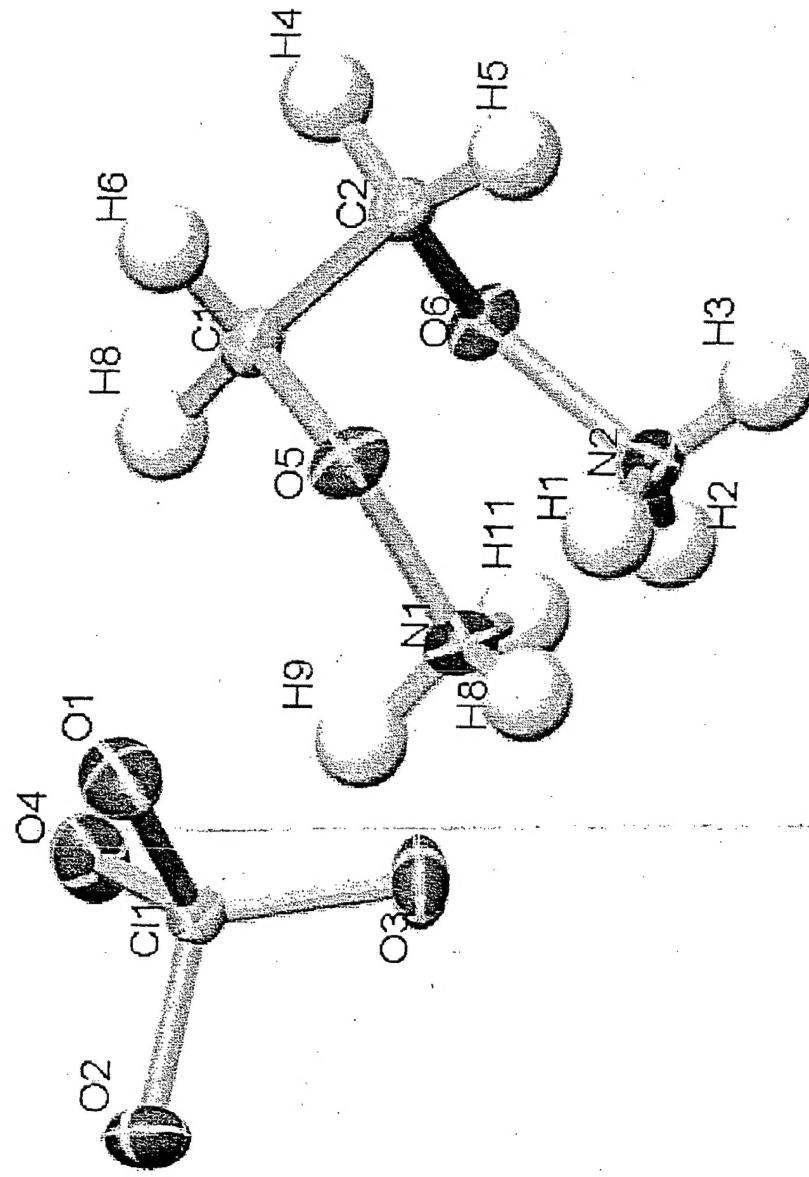
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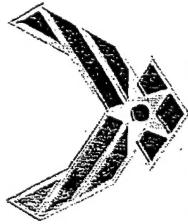


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X-ray diffraction confirmed structure, lots of hydrogen bonding!
H(1) and H(8) are partial occupancy 70%/30%

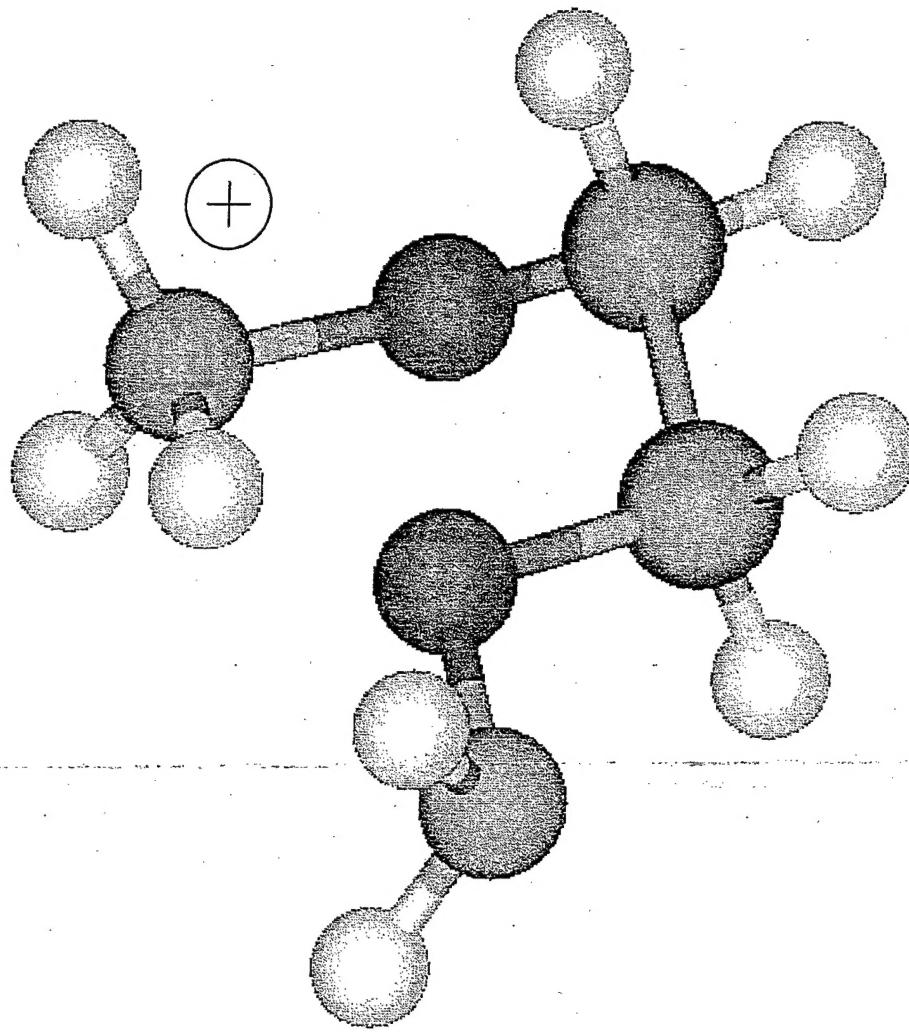




AFRL Ionic Liquids

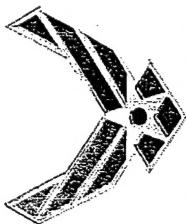


High level computational studies (Dr. Jeff Sheehy NASA/Marshall) revealed a slightly different structure. Comparison of bond distances matched well though

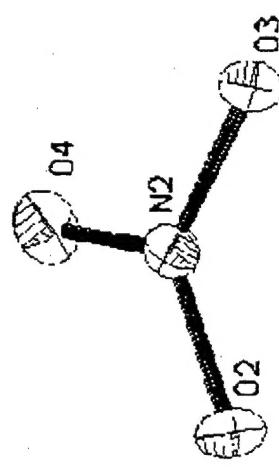
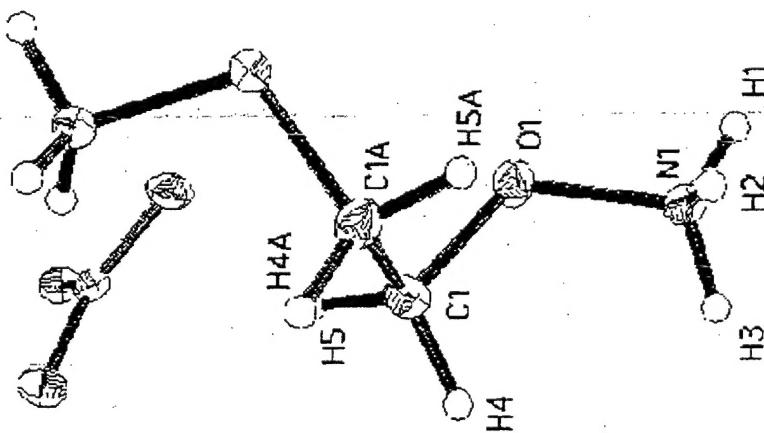




AFRL Ionic Liquids

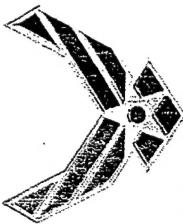


X-ray structure ethylene bisoxymine dinitrate was also solved

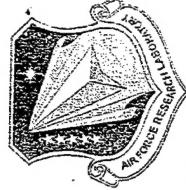


Drake, G.; Hawkins, T.; Hall, L.; Sheehy, J. Prop. Energ. Pyrotech. Submitted 2004.

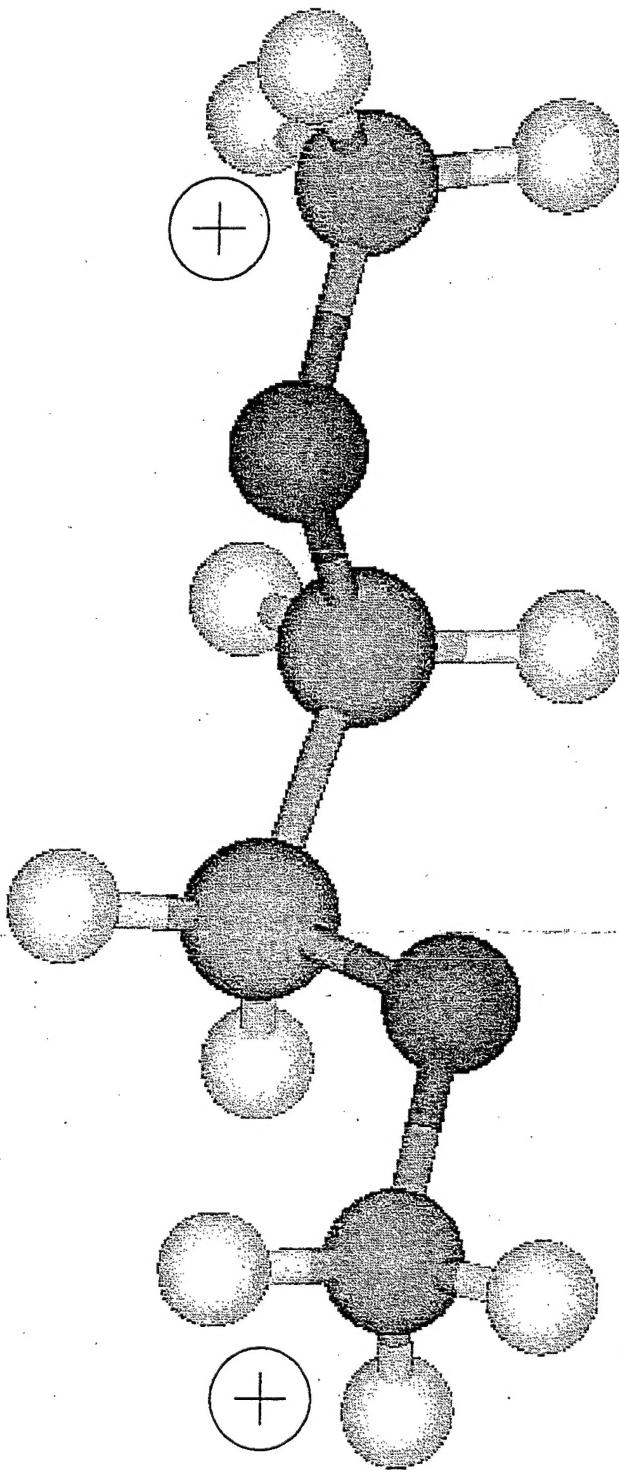
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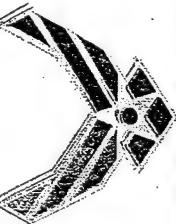
AFRL Ionic Liquids



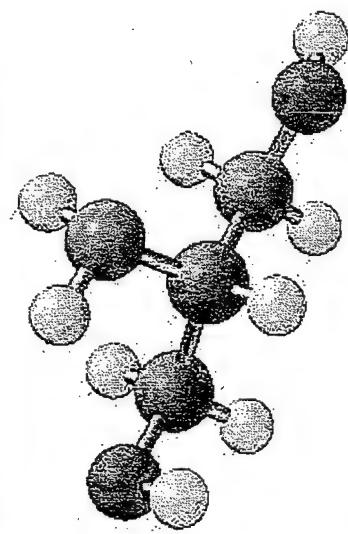
High level calculations (Jeff Sheehy) of the gas phase ethylene bisoxyammonium Dication revealed a similar structure with accurately predicted bond distances.



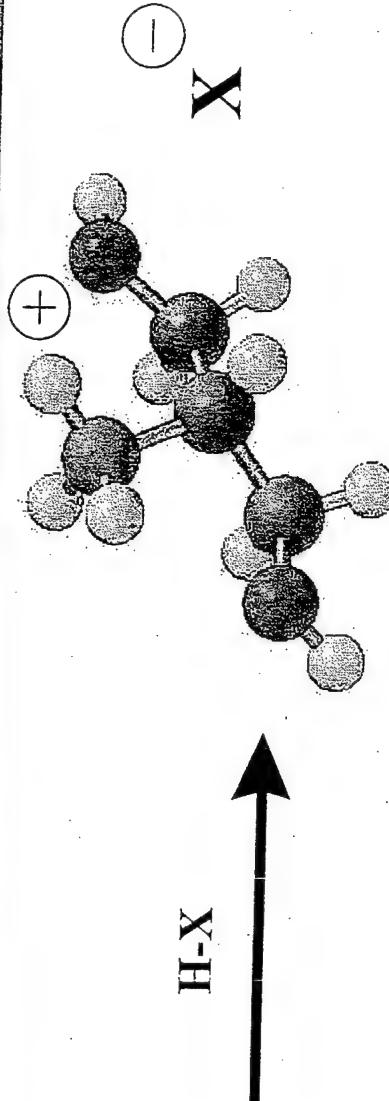
Drake, G.; Hawkins, T.; Hall, L.; Sheehy, J. Prop. Energ. Pyrotech. Submitted 2004.
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1,3-dihydroxy-2-aminopropane
(serinol)



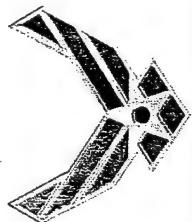
$\text{X}^- = \text{NO}_3^- , \text{ClO}_4^- , \text{N}(\text{NO}_2)_2^-$

| Salt | m.p. | DSC onset | Impact (kg·cm) | Friction (kg) |
|---------------------|----------|-----------|----------------|---------------|
| Serinol nitrate | 61-66° C | 215° C | 180 | 18.0 |
| Serinol perchlorate | 55-60° C | 250° C | 200 | >37.8 |
| Serinol dinitramide | 41-44° C | 135° C | 16 | 23.4 |

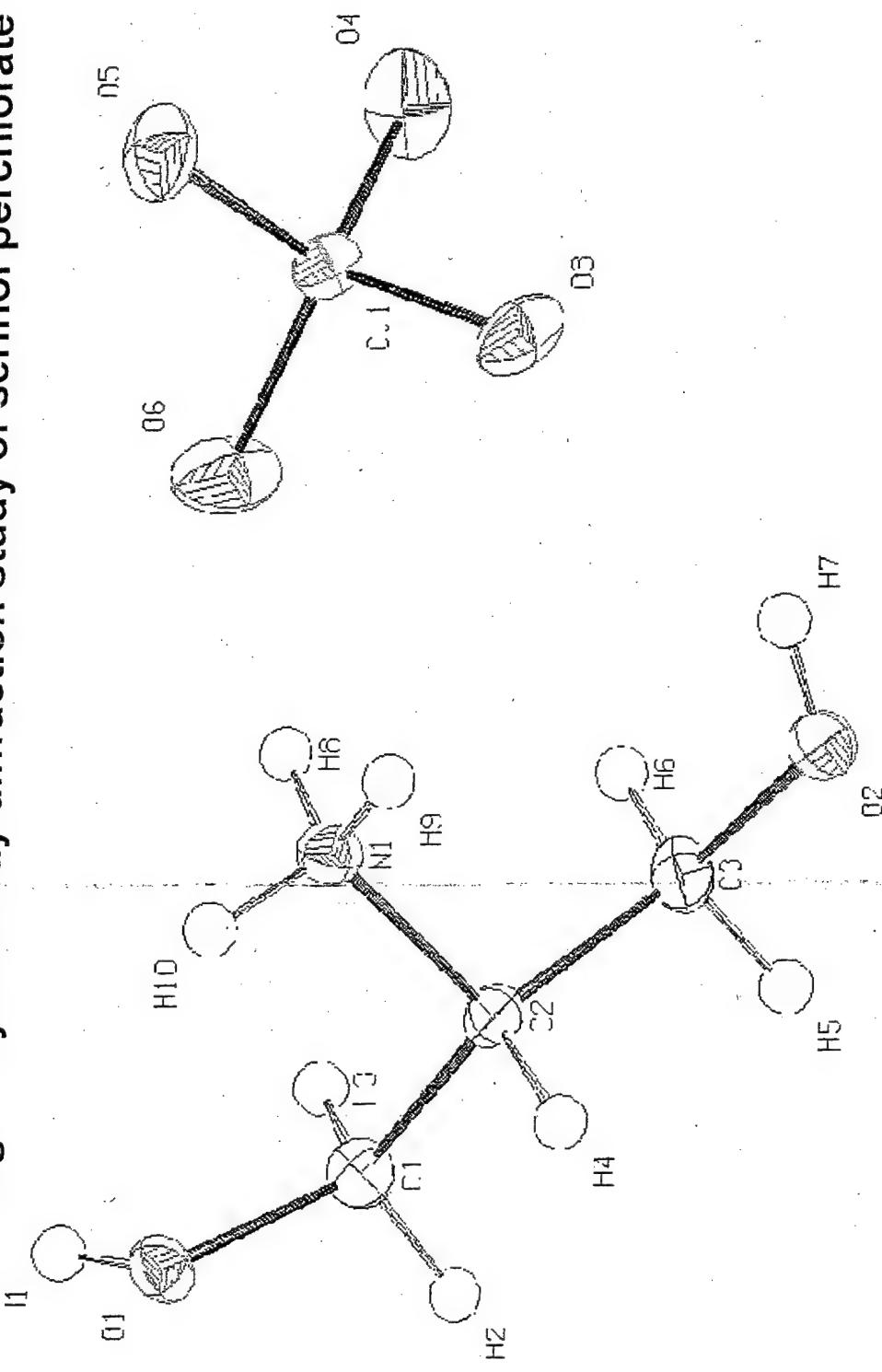
Drake, G.; Hawkins, T.; Tolison, K.; Hall, L.; Boatz, J. Prop. Energ. Pyrotech. 2004 submitted.
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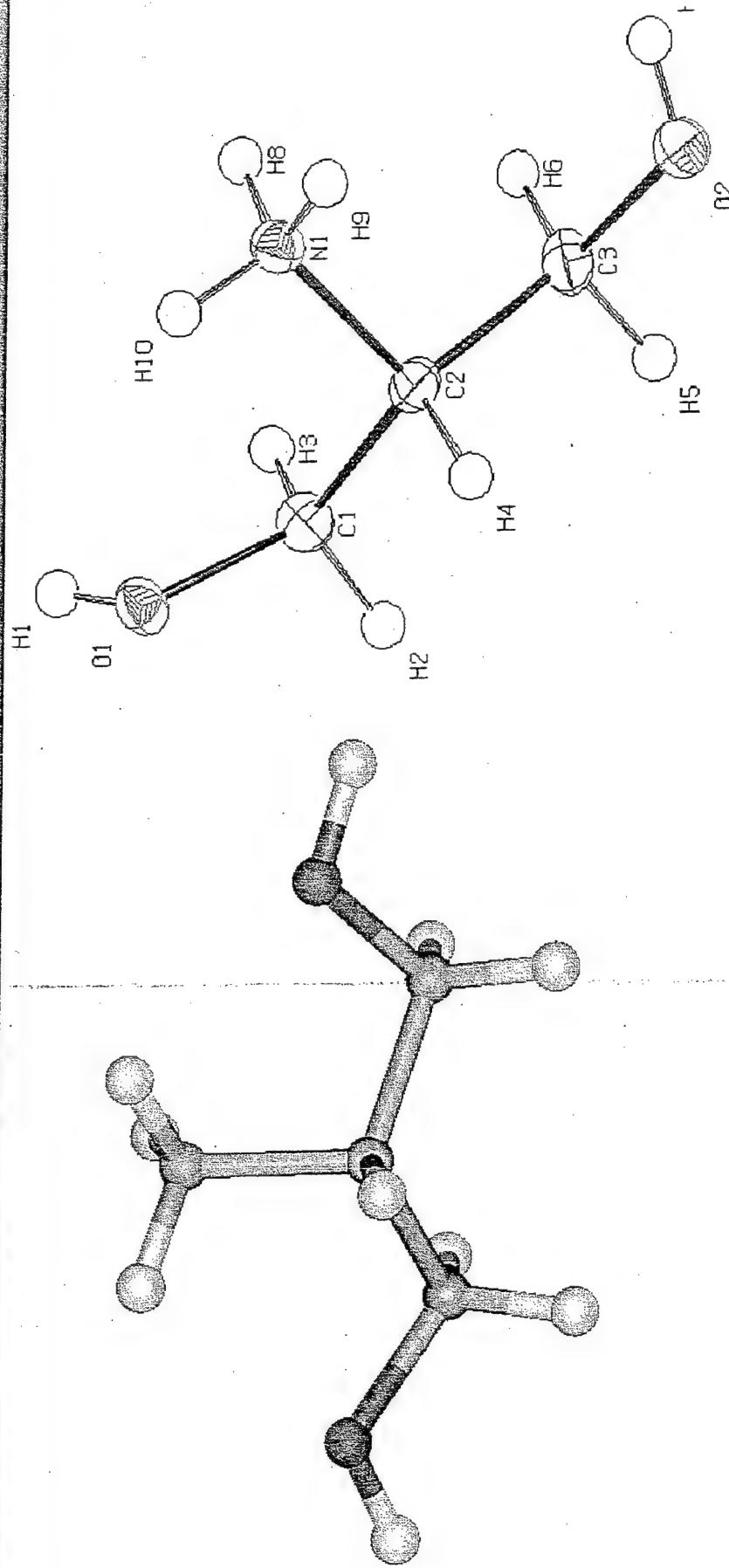
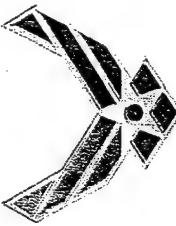


Single Crystal x-ray diffraction study of serinol perchlorate

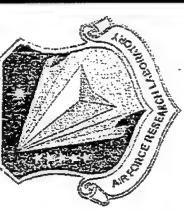


Drake, G.; Hawkins, T.; Tollison, K.; Hall, L.; Boatz, J. Prop. Energ. Pyrotech. 2004 submitted.
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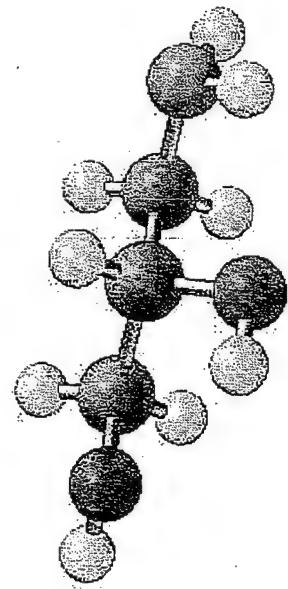
AFRL Ionic Liquids



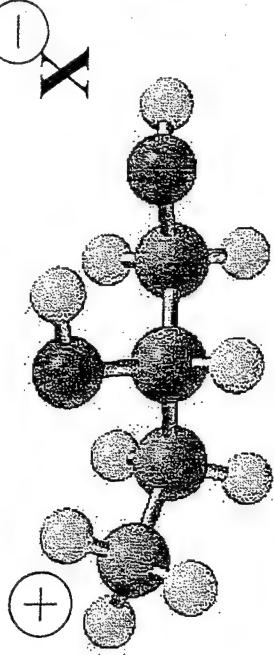
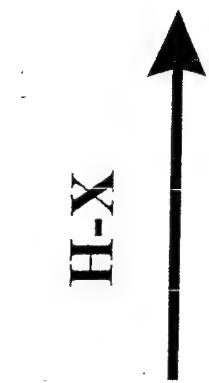
Theoretical computations by Dr. Jerry Boatz (AFRL) using B3LYP/6-31G(d,p) of serinol cation in the gas phase (C_s symmetry) as compared to that observed In the single crystal x-ray diffraction study of serinol perchlorate



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H-X



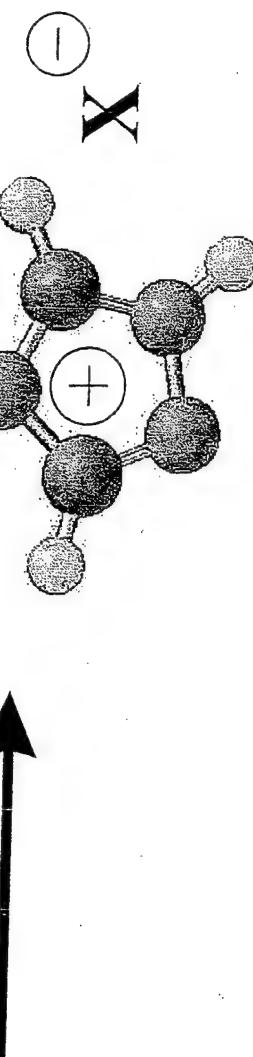
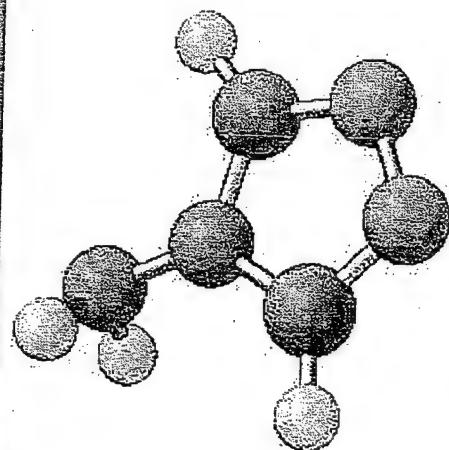
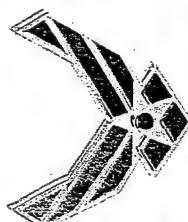
1,2-dihydroxy-3-aminopropane
(chiral)

$$X^- = \text{NO}_3^-, \text{ClO}_4^-, \text{N}(\text{NO}_2)_2^-$$

| <u>SALT</u> | <u>Melting Point</u> | <u>Decomposition Onset</u> |
|--|----------------------|----------------------------|
| 1,2-dihydroxy-3-aminopropane nitrate | -40° C | 220° C |
| 1,2-dihydroxy-3-aminopropane perchlorate | ? | 225° C |
| 1,2-dihydroxy-3-aminopropane dinitramide | -5° C | 135° C |



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4-amino-1,2,4-triazole



| SALT | Melting Point | Decomposition Onset | Impact kg/cm |
|--------------------------------------|---------------|---------------------|-----------------|
| 4-amino-1,2,4-triazolium nitrate | 69° C | 180° C | >200 |
| 4-amino-1,2,4-triazolium perchlorate | 84° C | 210° C | 30 |
| 4-amino-1,2,4-triazolium dinitramide | 20° C | 145° C | <5 |

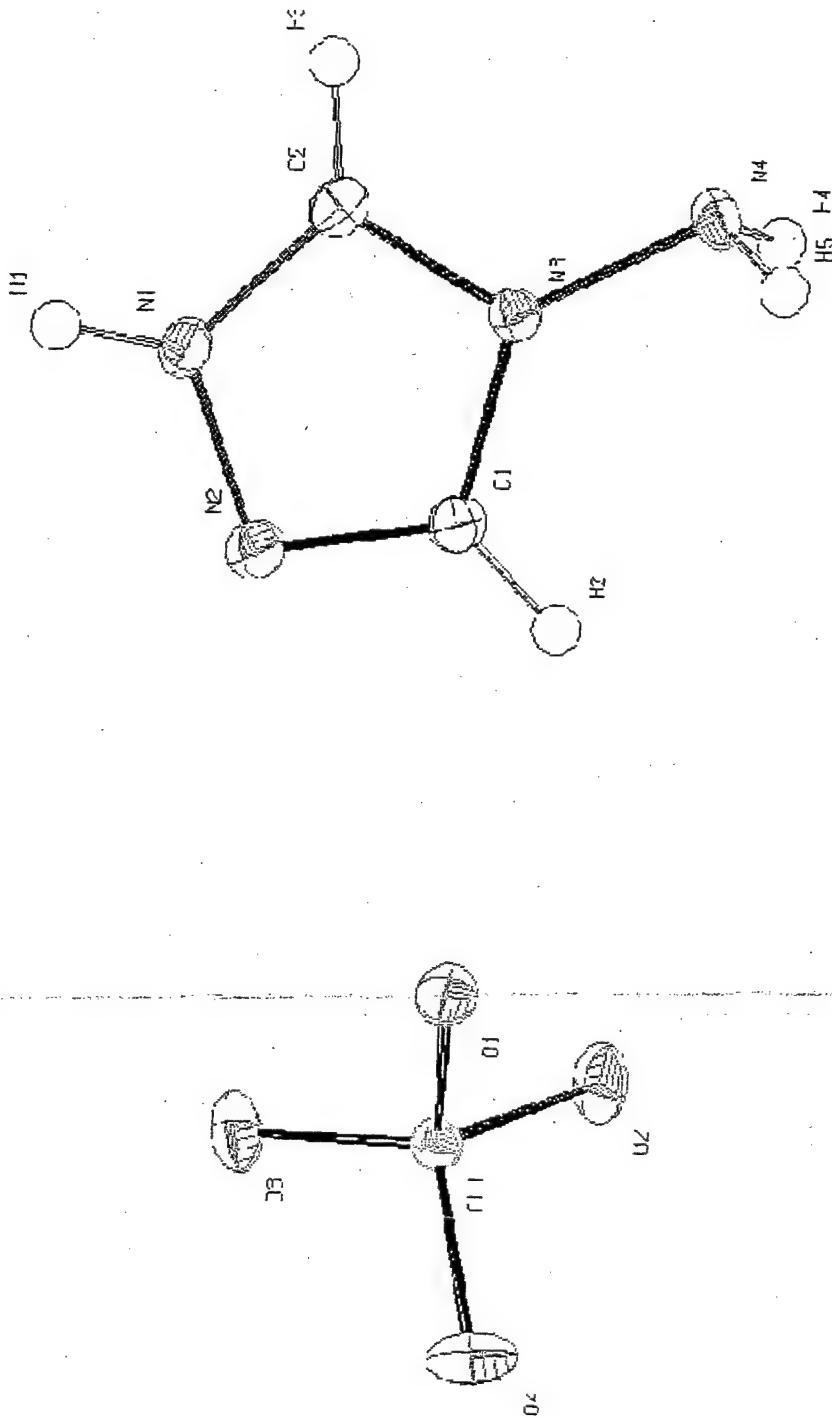
Drake, G.; Hawkins, T.; Brand, A.; Hall, L.; McKay, M.; Vij, A.; Ismail, I. Prop. Expl. Pyrotech. 2003, 28, 174.
"Distribution A. Public Release, Distribution unlimited."



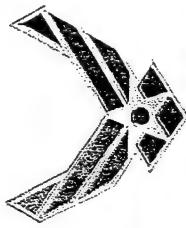
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Single crystal x-ray diffraction study revealed the expected structure for 4-amino-1,2,4-triazolium perchlorate.

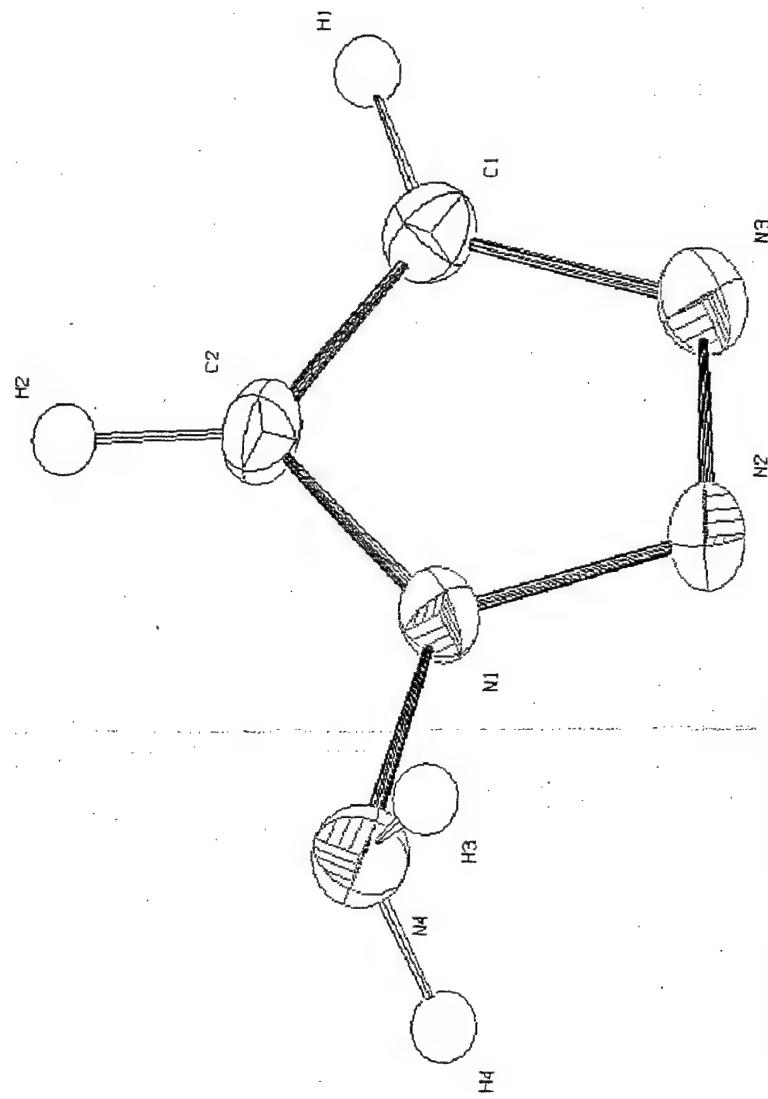
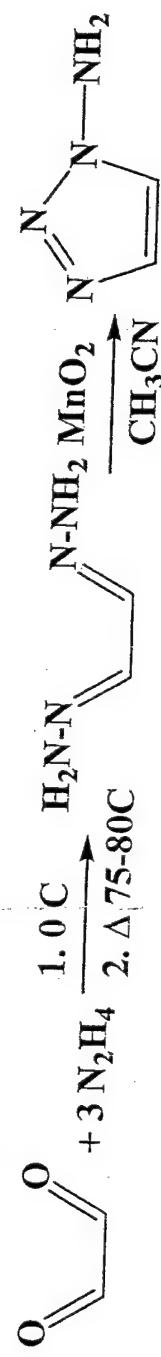


Hall, L.; Drake, G. Unpublished results 2004.
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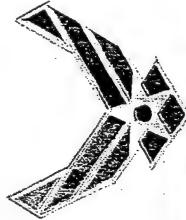
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New Effort with 1-amino-1,2,3-triazole



Kaplan, G.; Drake, G.; Hawkins, T.; Tollison, K.; Hall, L. J. Heterocyc. Chem. submitted 2004.

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Synthesis of 1-amino-3-alkyl-1,2,3-triazolium halides

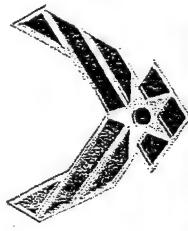


| New Salt | M.P. (°C) | Decomp. |
|---|-----------|---------|
| 1-amino-3-methyl-1,2,3-triazolium iodide | 146 | 150 |
| 1-amino-3-ethyl-1,2,3-triazolium bromide | 118 | 149 |
| 1-amino-3-propyl-1,2,3-triazolium bromide | 128 | 135 |
| 1-amino-3-allyl-1,2,3-triazolium bromide | 100 | 135 |
| 1-amino-3-butyl-1,2,3-triazolium bromide | 131 | 145 |

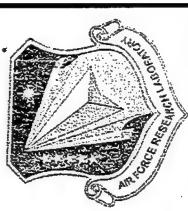
Not Ionic Liquids!

Kaplan, G.; Drake, G.; Hawkins, T.; Tollison, K.; Hall, L. J. *Heterocyc. Chem.* submitted 2004.

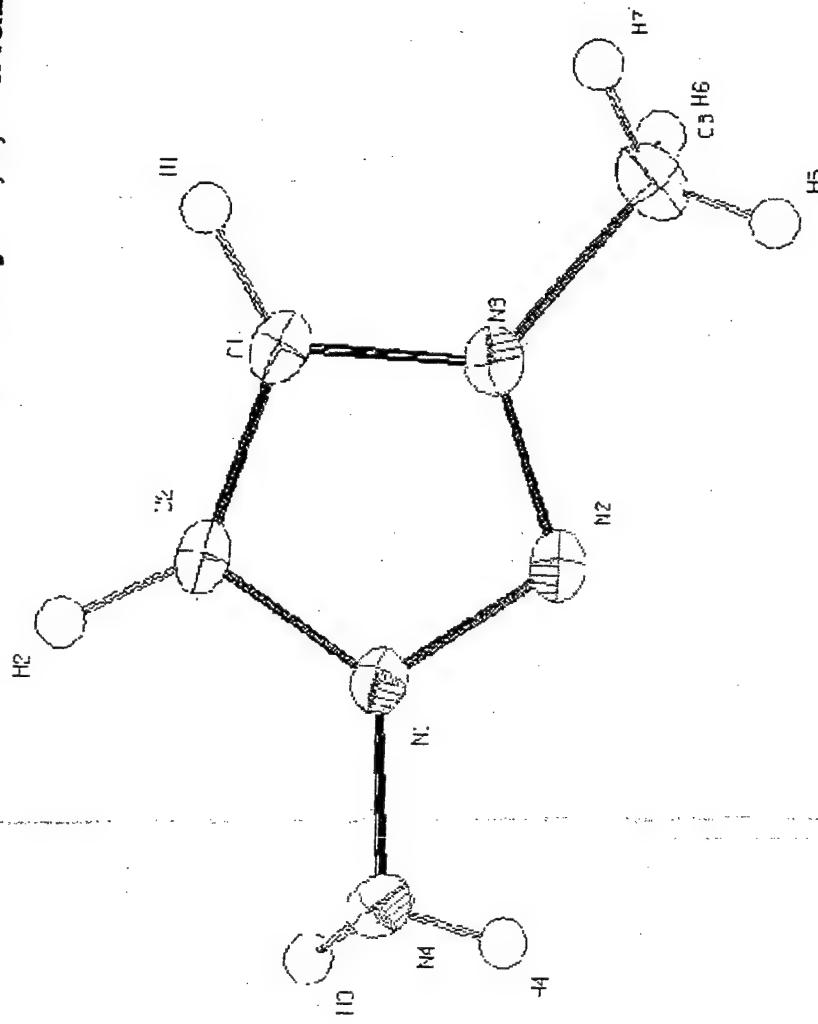
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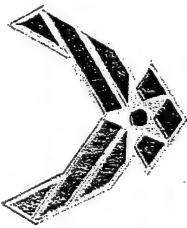
Single crystal x-ray diffraction study of 1-amino-3-methyl-1,2,3-triazolium iodide



11

Kaplan, G.; Drake, G.; Hawkins, T.; Tollison, K.; Hall, L. J. Heterocyc. Chem. submitted 2004.

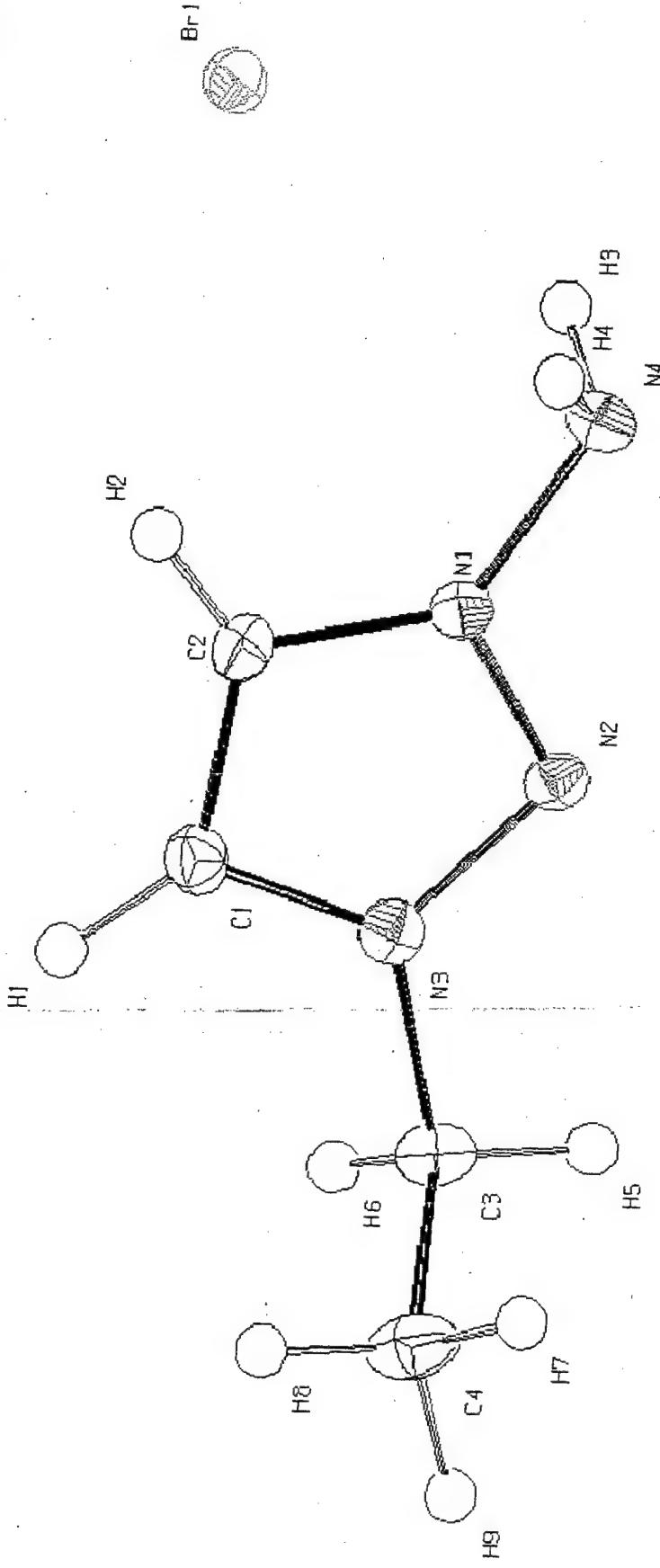
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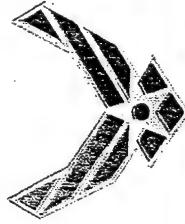


Single crystal x-ray diffraction study of 1-amino-3-ethyl-1,2,3-triazolium bromide



Kaplan, G.; Drake, G.; Hawkins, T.; Tollison, K.; Hall, L. J. Heterocyc. Chem. submitted 2004.

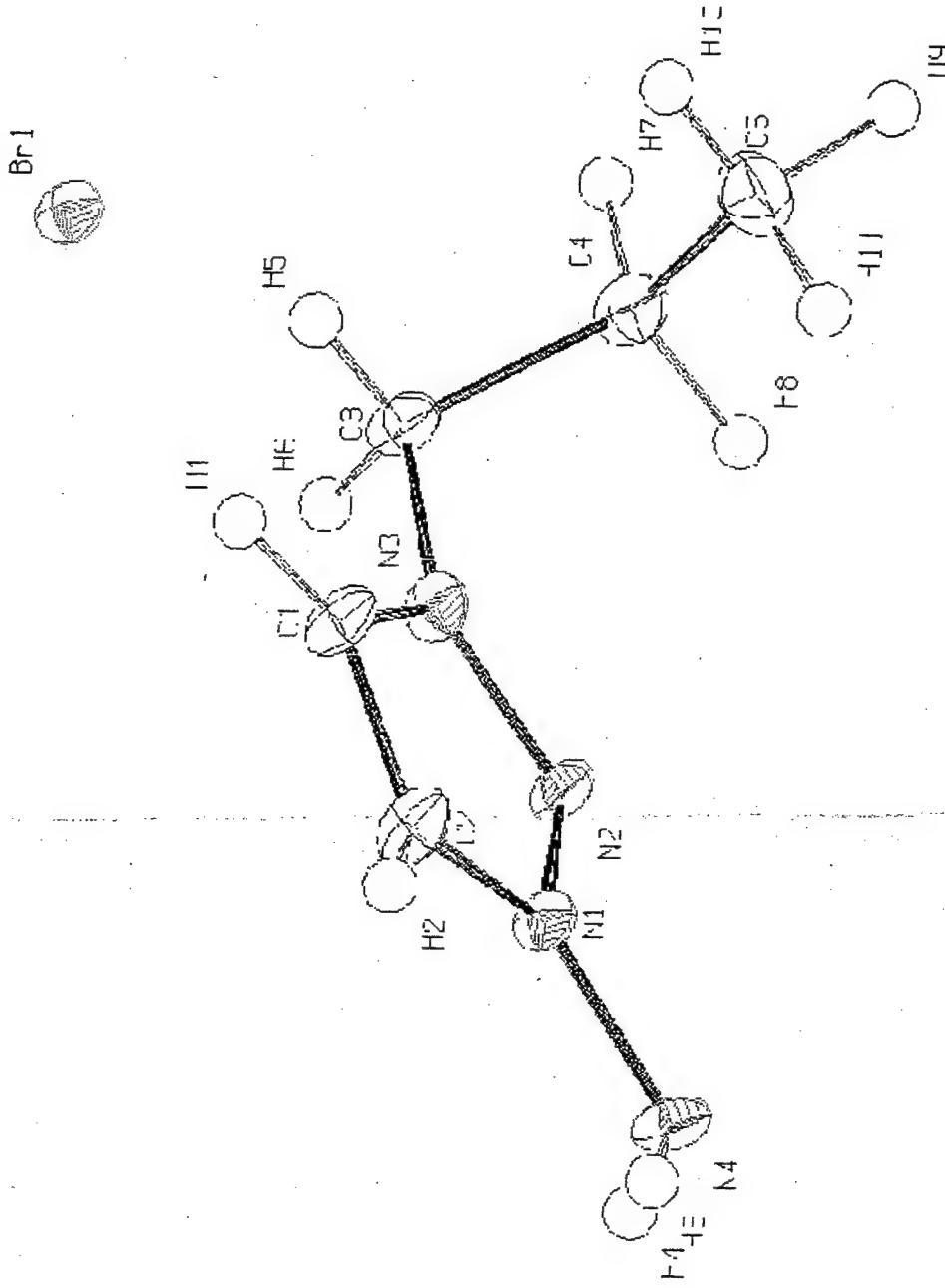
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Single crystal x-ray diffraction study of 1-amino-3-propyl-1,2,3-triazolium bromide



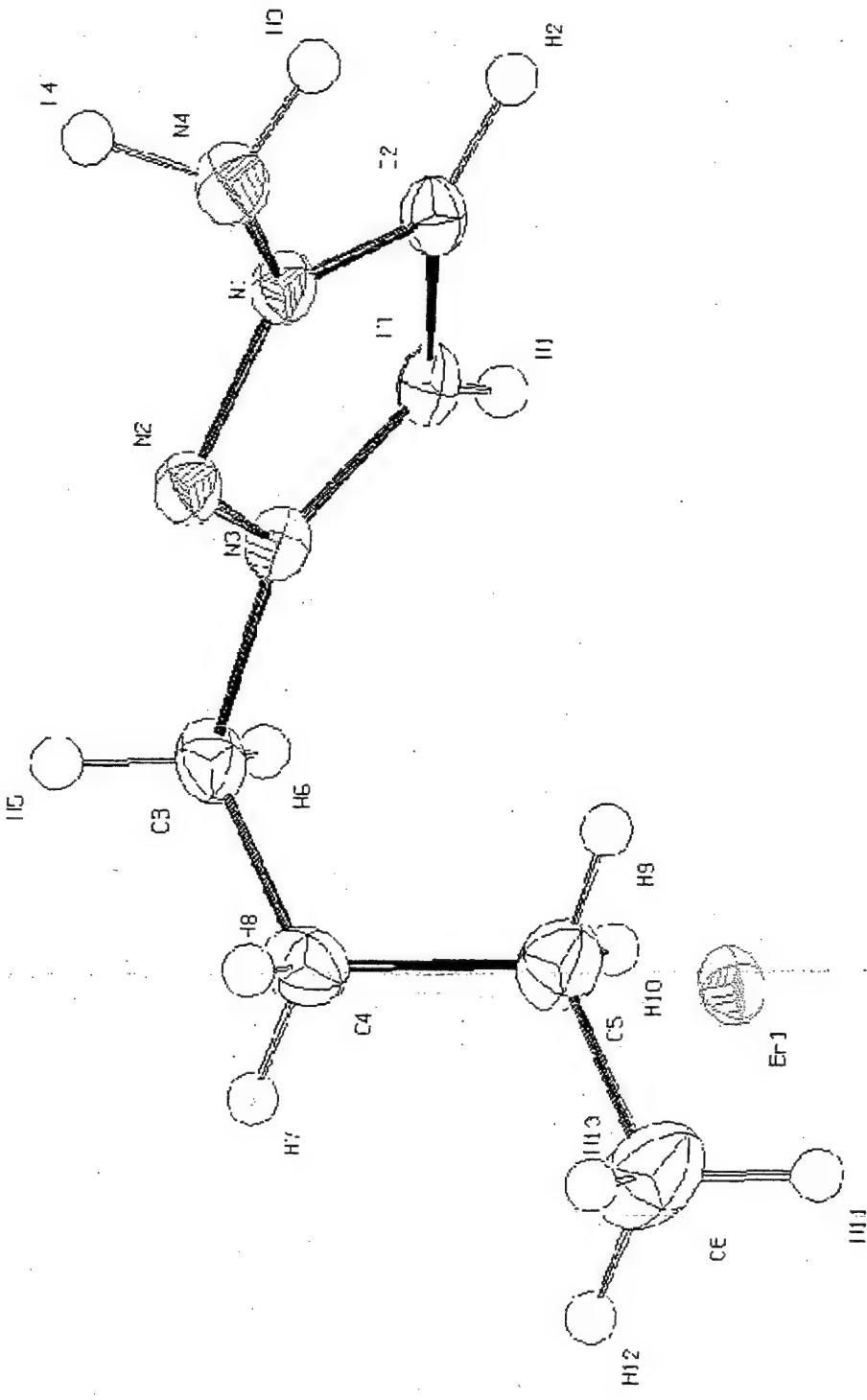
Kaplan, G.; Drake, G.; Hawkins, T.; Tollison, K.; Hall, L. J. Heterocyc. Chem. submitted 2004.
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Single crystal x-ray structure of 1-amino-3-butyl-1,2,3-triazolium bromide



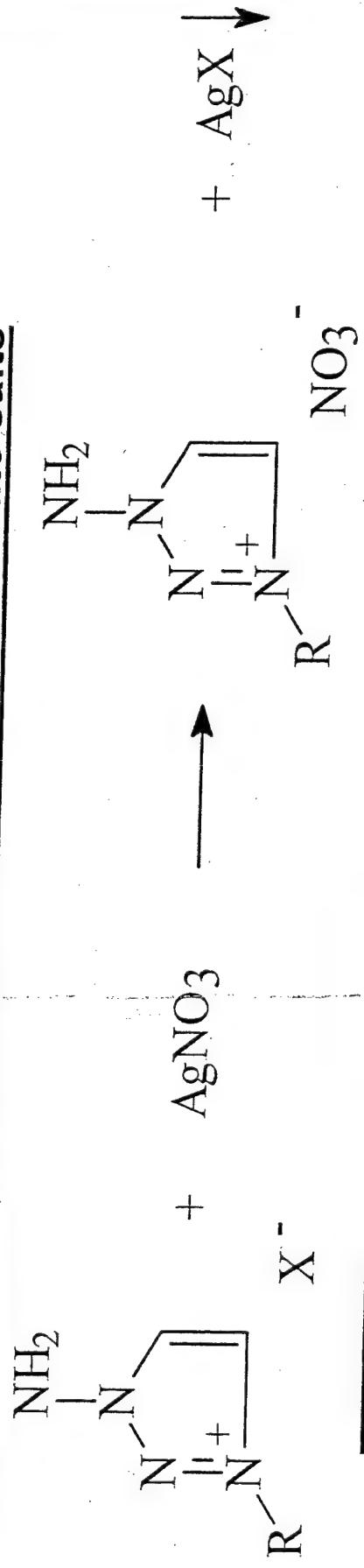
Kaplan, G.; Drake, G.; Hawkins, T.; Tollison, K.; Hall, L. J. Heterocyc. Chem. submitted 2004.

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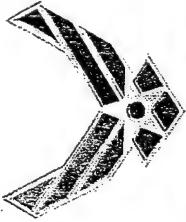
AFRL Ionic Liquids

Straight-forward metathesis forms desired nitrate salts



| <u>NEW SALT</u> | M.P. (°C) |
|---|-----------|
| 1-amino-3-methyl-1,2,3-triazolium nitrate | 86 |
| 1-amino-3-ethyl-1,2,3-triazolium nitrate | 30 |
| 1-amino-3-propyl-1,2,3-triazolium nitrate | 33 |
| 1-amino-3-allyl-1,2,3-triazolium nitrate | 8 |
| 1-amino-3-butyl-1,2,3-triazolium nitrate | 48 |

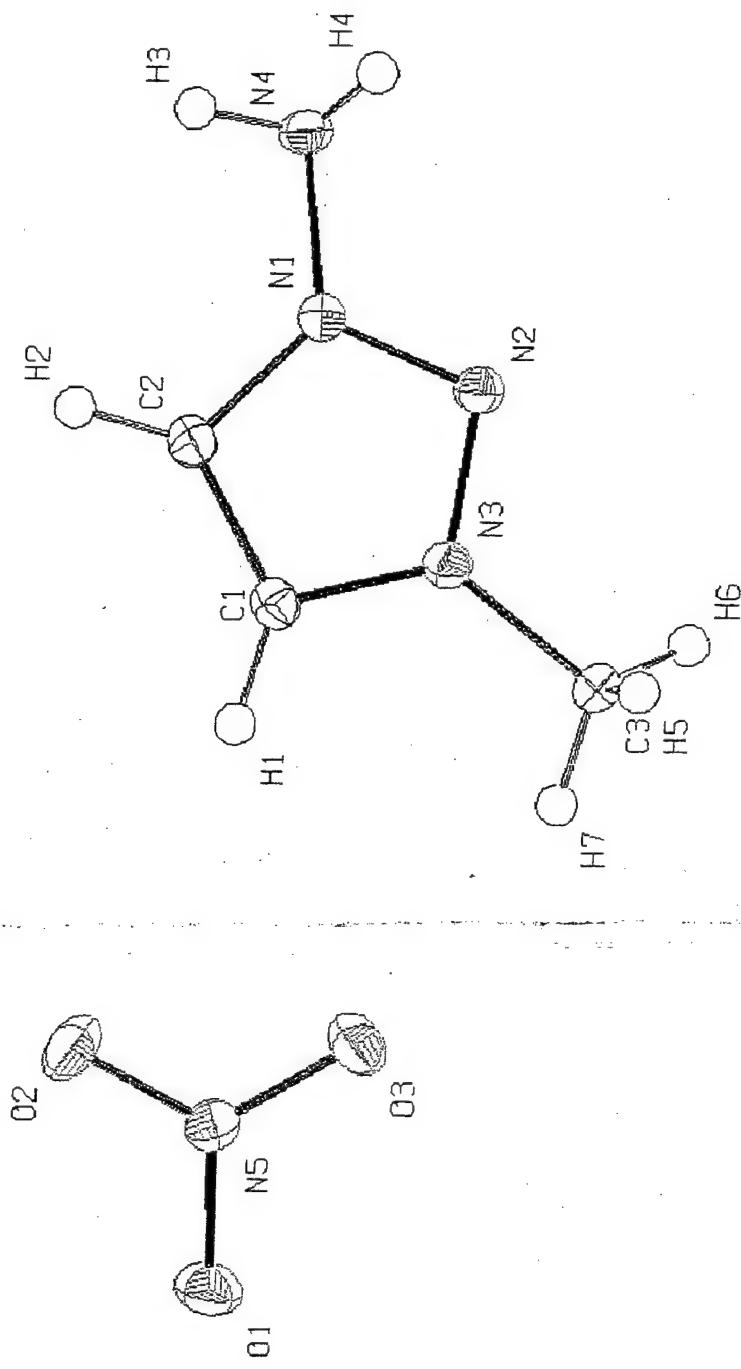
Kaplan, G.; Drake, G.; Tollison, K.; Hawkins, T.; Hall, L. Manuscript in progress 2004.
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AFRI Ionic Liquids



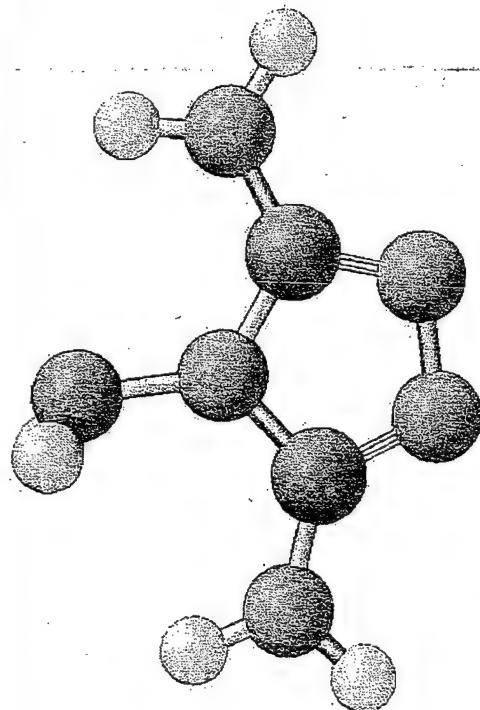
Single crystal x-ray diffraction study of 1-amino-3-methyl-1,2,3-triazolium nitrate



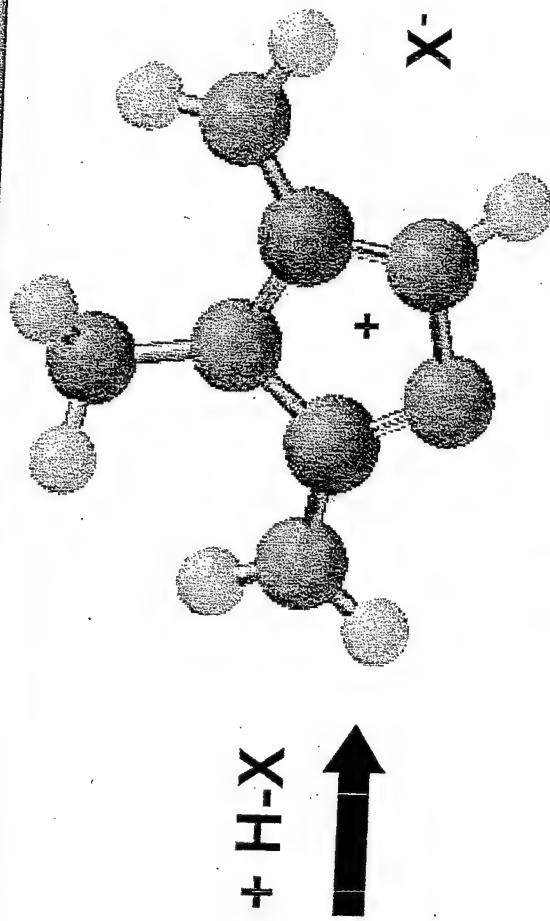
Kaplan, G.; Drake, G.; Hawkins, T.; Hall, L.; Tollison, K. Manuscript in progress 2004
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3,4,5-triamino-1,2,4-triazole
(Guanazine)

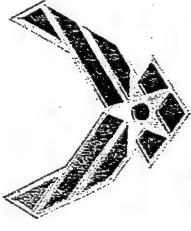


$X^- = NO_3^-, ClO_4^-, N(NO_2)_2^-$

| New Salt | M.P. (°C) | Impact (kgcm) | Friction (Kg) |
|-------------------------|-----------|---------------|---------------|
| Guanazinium nitrate | 225 | 200 | 16 |
| Guanazinium perchlorate | 215 | 50 | 15.2 |
| Guanazinium dinitramide | 145 | 196 | 15.2 |

Not Ionic Liquids!

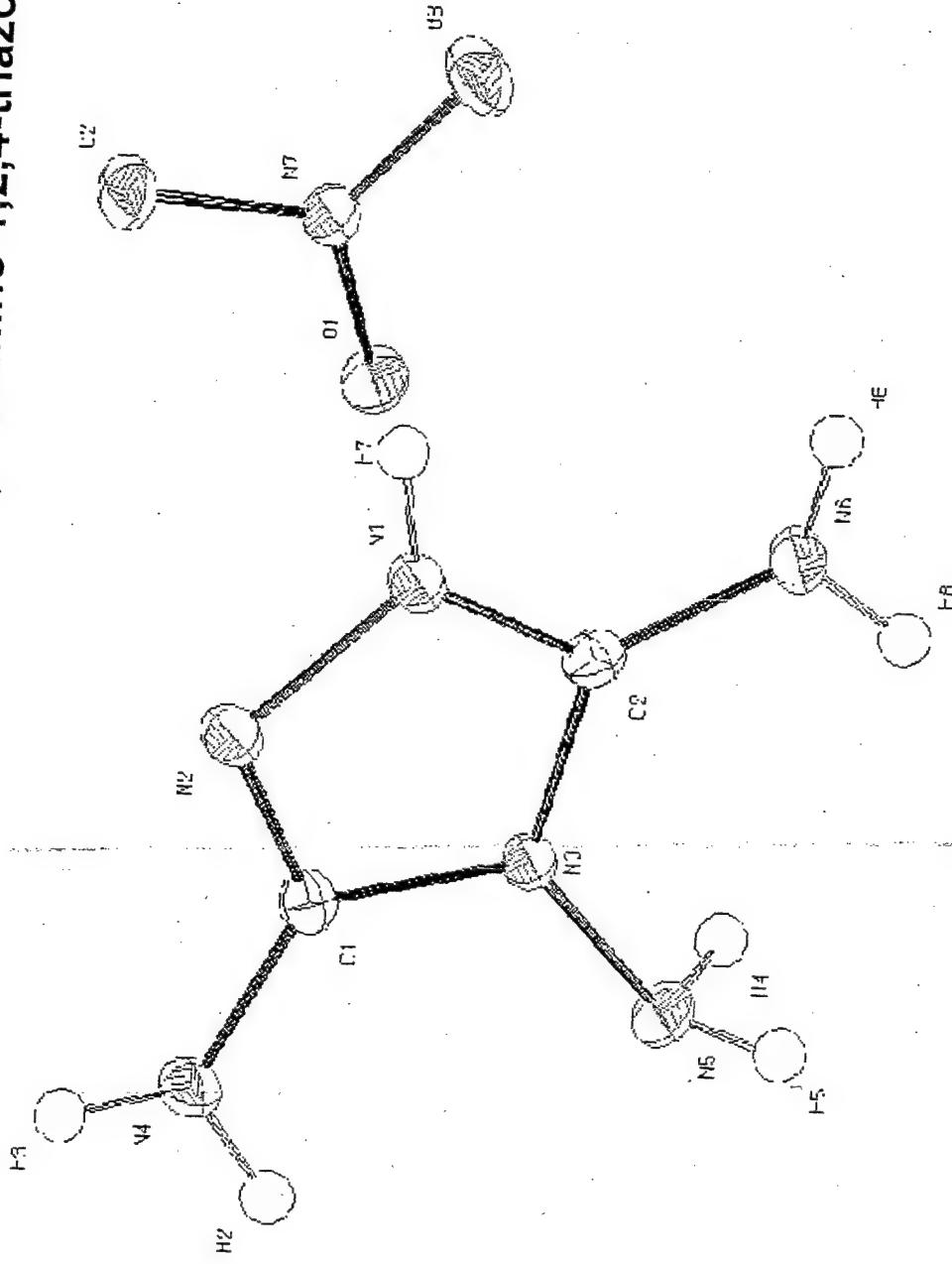
Drake, G.; Hawkins, T.; Hall, L.; Brand, A. Prop. Expl. Pyrotech. 2004, to be submitted
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AFRL Ionic Liquids

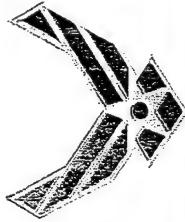


Single crystal x-ray diffraction study of 3,4,5-triamino-1,2,4-triazolium nitrate



Drake, G.; Hawkins, T.; Hall, L.; Brand, A. Prop. Expl. Pyrotech. 2004, to be submitted

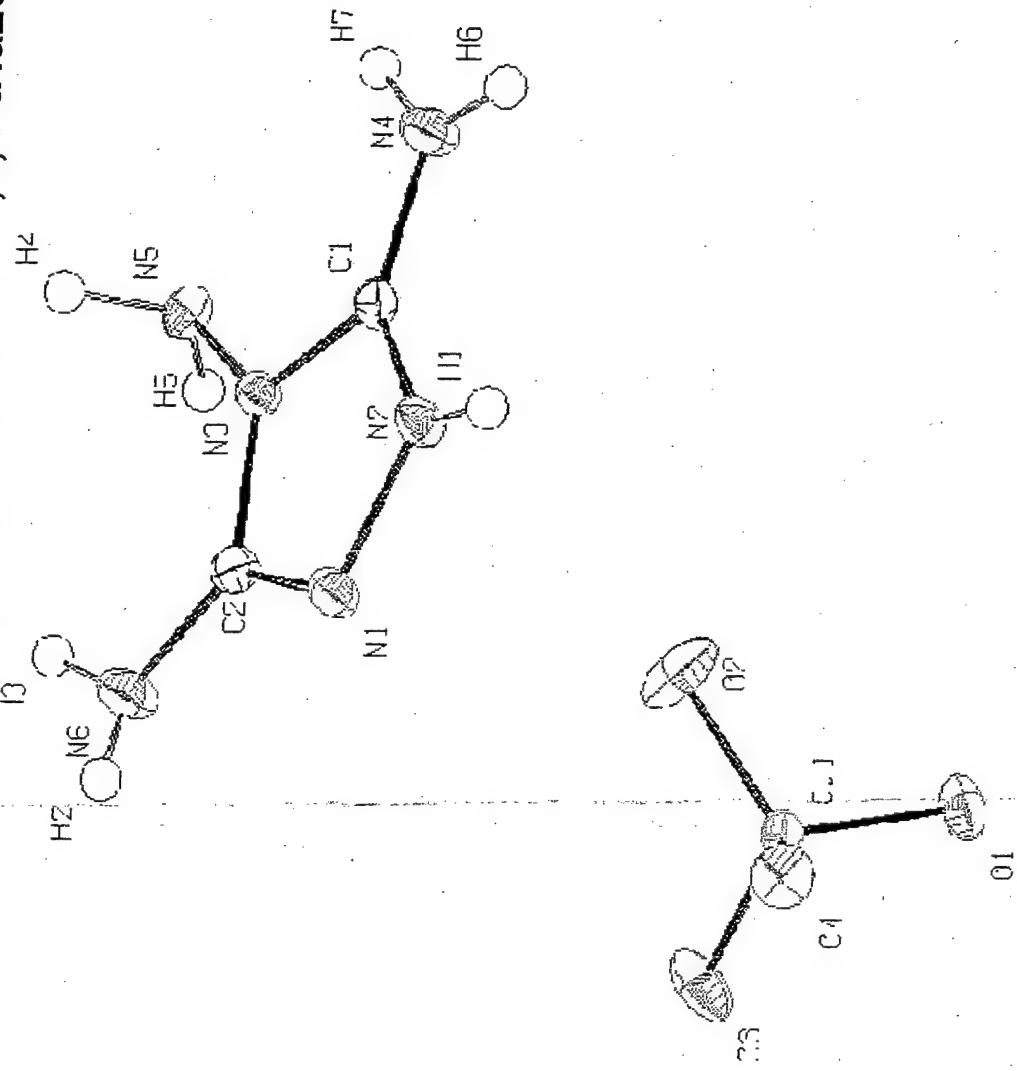
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Single crystal x-ray diffraction study of 3,4,5-triamino-1,2,4-triazolium perchlorate



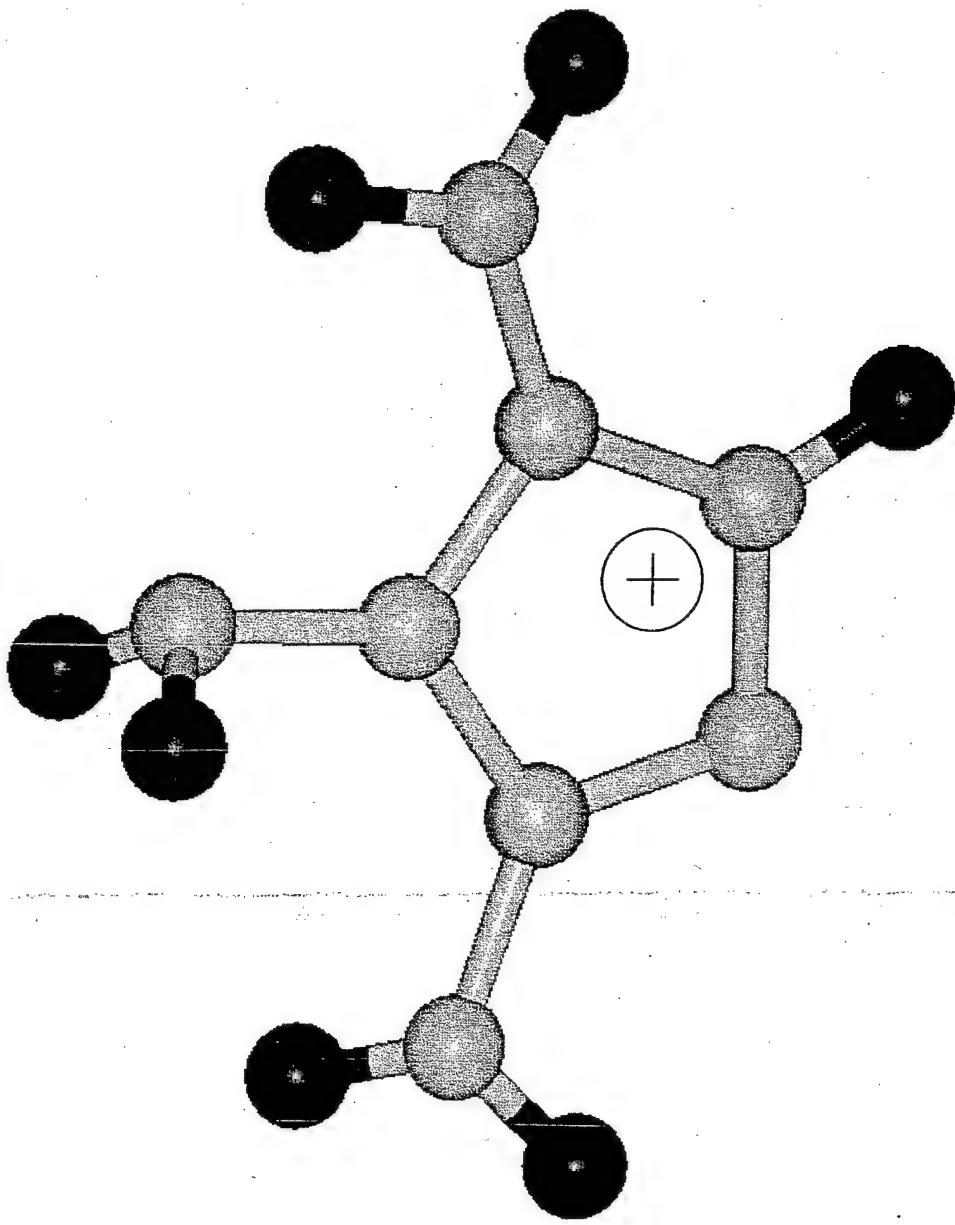
Drake, G.; Hawkins, T.; Boatz, J.; Hall, L.; Brand, A. Prop. Expl. Pyrotech. 2004, to be submitted
Distribution A. Public Release, Distribution unlimited



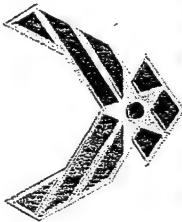
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Theoretical Calculations of protonated 3,4,5-triamino-1,2,4-triazole



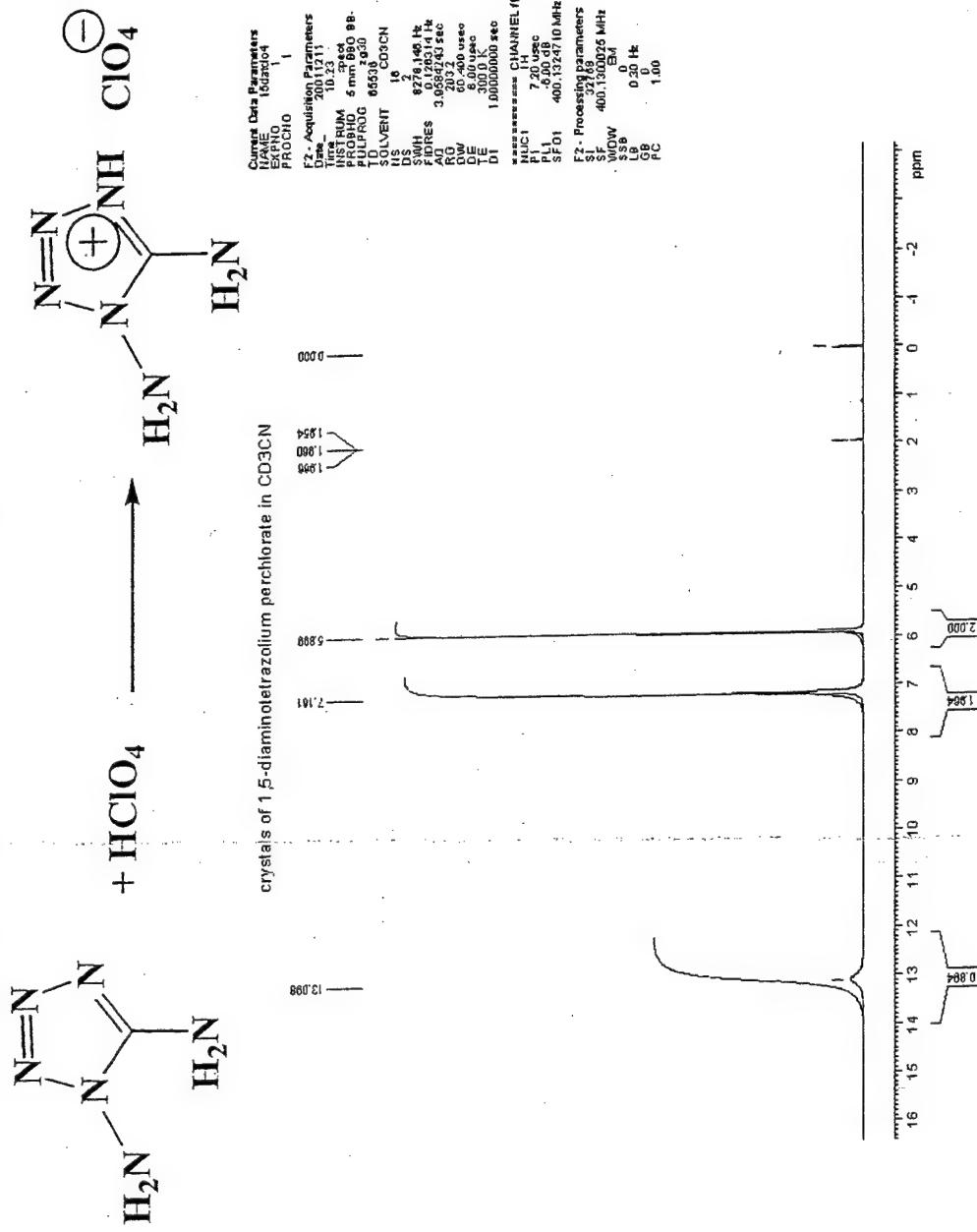
Drake, G.; Hawkins, T.; Boatz, J; Hall, L.; Brand, A. Prop. Expl. Pyrotech. 2004, to be submitted
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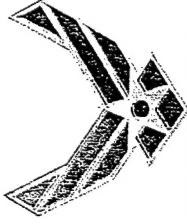


Experimental points to proton going on tetrazole ring, which disagrees from Russian findings



P. Gaponik; V. Karavaï "Synthesis and properties of 1,5-diaminotetrazole" Khim. Geterotsikl. Soedin. 1984, 1683.

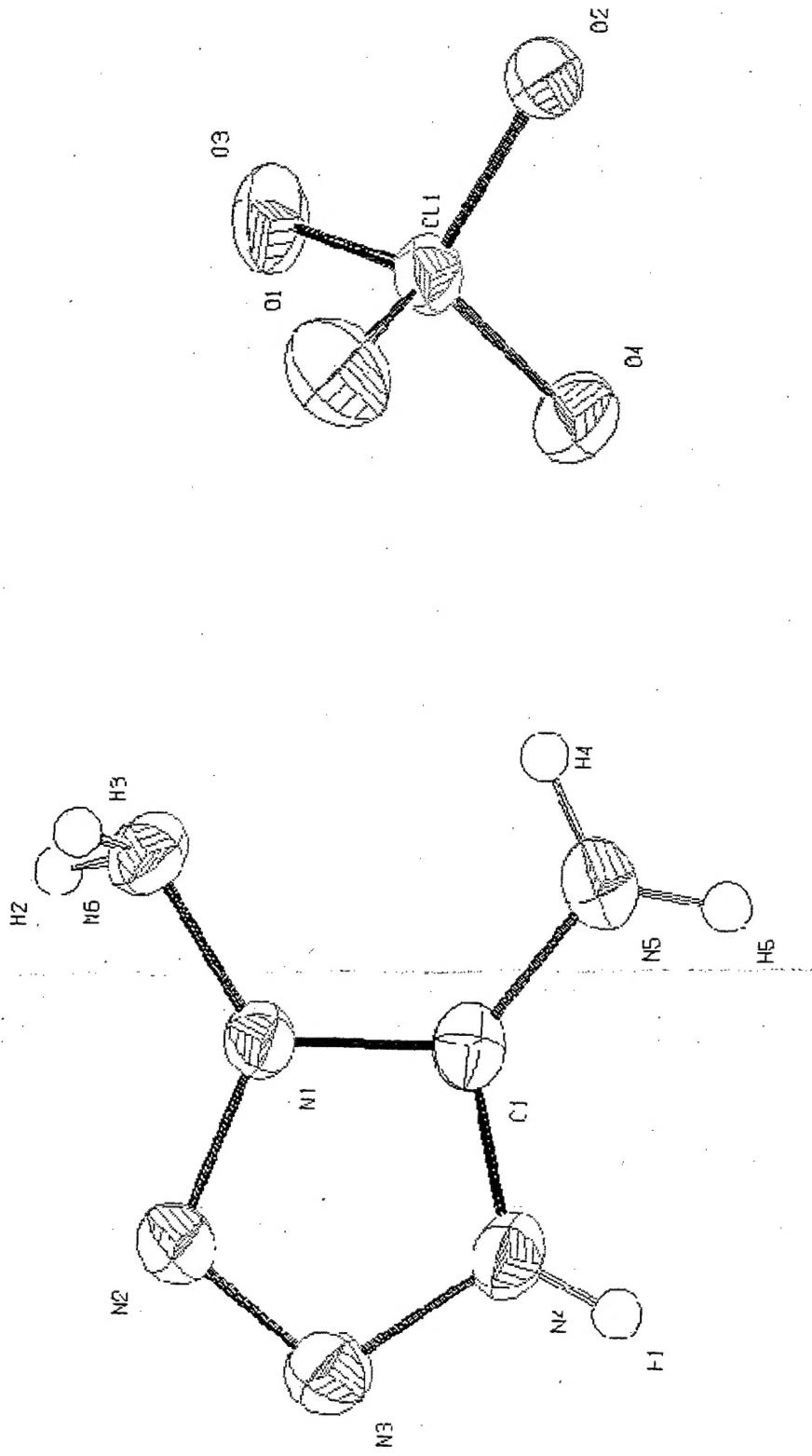
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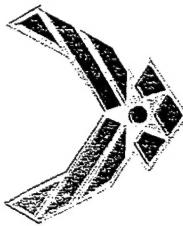


Single crystal X-ray diffraction study of 1,5-diamino-1,2,3,4-tetrazolium perchlorate

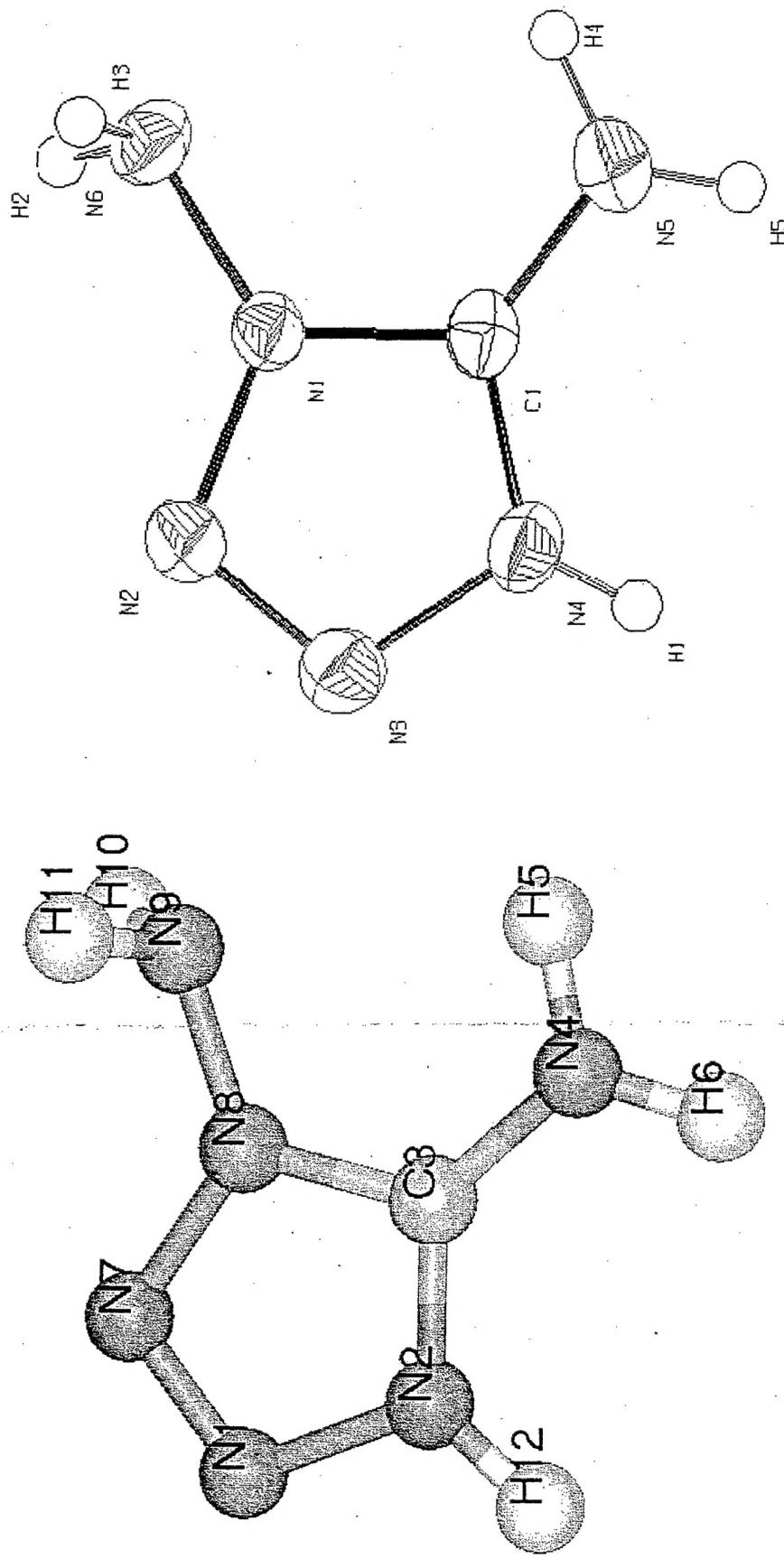


Drake, G.; Hawkins, T.; Vij, A.; Hall, L.; Boatz, J. Prop. Explos. Pyro. 2004, Submitted

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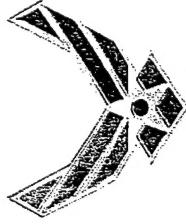


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Theory and Experimental Structures of 1,5-diamino-1,2,3,4-tetrazolium perchlorate
are in close agreement in distances and angles.

Drake, G.; Hawkins, T.; Vlij, A.; Hall, L.; Boatz, J. Prop. Explos. Pyro. 2004, Submitted
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Summary and Conclusions

Hydrogen bonding is highly important in all systems

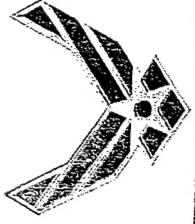
Asymmetry can dramatically affect physical properties and modest changes can have drastic affects.

N-amino heterocycles offer a rich platform for ionic liquids

New triazole and tetrazole systems have been identified as ionic liquid precursors

X-ray crystallography continues to be a powerful tool in identifying interactions in the solid state.

There are a lot of possibilities out there that await development....



AFRL Ionic Liquids

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